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14. ABSTRACT <p>The third quarter of FY2001 has been devoted to the determination of creep behavior of the one of the two categories of materials produced by this project-silicon nitride/silicon carbide micro-nano composite sintered by Spark Plasma Sintering (SPS). The microstructural details highlight the characteristics of (1) existing of turbostratic graphite phase at the intergranular regions; (2) the non-equilibrium distribution of glassy phases. The creep curves show a distinct stage of steady state creep, and investigations under varied temperature and stress level show stress exponent of 0.7-2.0 and activation energy of about 400-800kJ/mol.</p>					
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# OFFICE OF NAVAL RESEARCH      Quarterly Report

**Term: 07/01/2001~09/30/2001**

## Contract Information

Contract Number	N00014-00-1-0186
Title of Research	Creep Behavior of Polymer Precursor Derived Si <sub>3</sub> N <sub>4</sub> /SiC Nanocomposites
Principal Investigator	Amiya K. Mukherjee
Organization	Department of Chemical Engineering and Materials Science, University of California, Davis

## Technical Section

### Technical Objectives

In the third quarter of FY2001, the specific objective is the creep resistance test of some of the silicon nitride and silicon carbide nanocomposites. The focus of this quarter has been on the micro-nano composite produced by SPS.

### Technical Approaches and Results

Micro-nano Si<sub>3</sub>N<sub>4</sub>/SiC composites were sintered by Spark Plasma Sintering (SPS), using polymer precursor pyrolysis-derived amorphous Si-C-N powders with yttria as the sintering aid. Ammonia treatment was conducted at the earlier stage of pyrolysis, at different temperatures, to provide different C/N ratio in the pyrolysis product and, therefore, varied Si<sub>3</sub>N<sub>4</sub>/SiC phase ratio in the sintered materials.

A summary of the types of materials batch-produced by the method of SPS for creep investigation is given in Table I.

**Table I      Summary of batch-produced sample materials for creep property evaluation**

SPS produced micro-nanocomposites					
Batch No	Ammonia-treatment	Nominal formula of 1450	Additive	High energy ball-milling	SPS procedure
NH0w	None	Si1.00C1.55 N0.81O0.17	8wt%Y <sub>2</sub> O <sub>3</sub>	WC	1600°C/10min
NH0F				Fe	
NH0S1				Si <sub>3</sub> N <sub>4</sub>	
NH0S2			5wt%Y <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub>	
NH400		Si1.00C1.55 N0.97O0.11	8wt%Y <sub>2</sub> O <sub>3</sub>	Fe	1600°C/10min

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NH500		Si1.00C1.29 N1.09O0.11	8wt%Y <sub>2</sub> O <sub>3</sub>	Fe	1500°C/10min
NH600		Si1.00C0.73 N1.29O0.11	8wt%Y <sub>2</sub> O <sub>3</sub>	Fe	1500°C/10min

Materials in Table I were machined into 4×4×7mm<sup>3</sup> specimens, and are being subjected to compression creep test under the temperature range 1250-1550°C and stress level 25-300MPa. Compression creep testing was done at Oak Ridge National Lab in Oak Ridge, Tennessee. Specimens were deformed using an Instron servo-mechanical test machine. A typical compression creep test setup is illustrated in Fig. 1. The load train consisted of two fully-dense  $\alpha$ -SiC pushrods, 19.05mm in diameter and 76mm long, attached to water cooled grips. The rectangular test specimen was compressed between free, axially aligned, flat and parallel ends of the SiC pushrods. The specimen and pushrods were then heated in air with molydisilicide heating elements to the setpoint temperature. Two thermocouples positioned close to the specimen were used to monitor and control the temperature to within  $\pm 3^\circ\text{C}$ . A high-temperature capacitive extensometer (25mm gauge length) was used to measure the mutual displacements of the SiC pushrods to a resolution of  $\pm 2\mu\text{m}$ . Displacement was measured as a function of time using a personal computer. Tests were terminated after 300-400 hours of secondary creep.

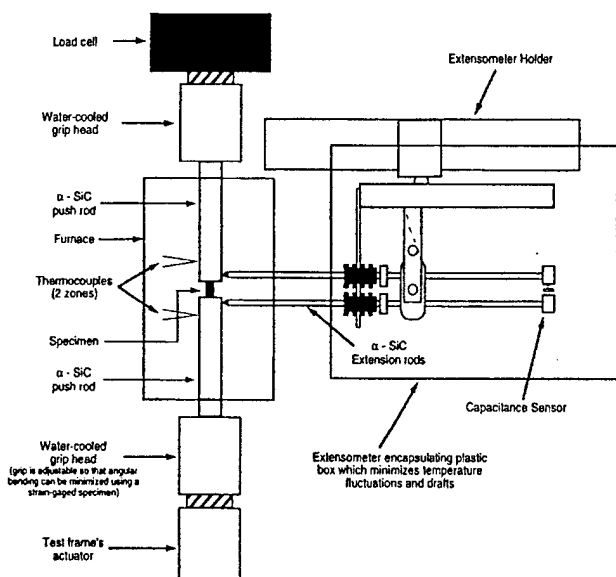


Fig.1 – Schematic of compression creep test setup.

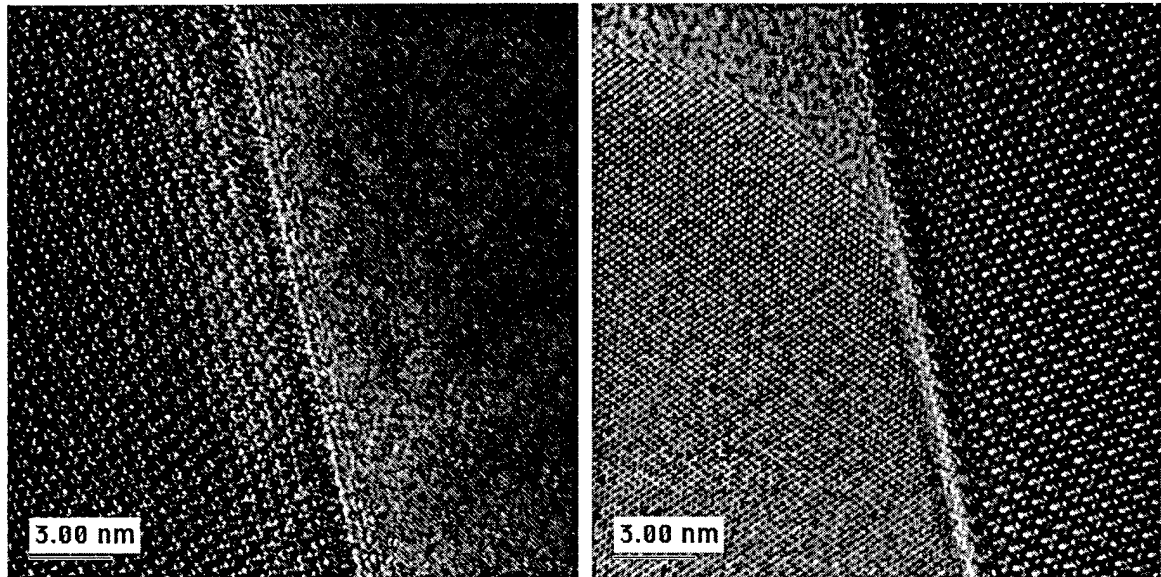
## Progress

### *Microstructural details of SPS-derived Si<sub>3</sub>N<sub>4</sub>/SiC nanocomposites*

In the 2000 Annual Report, we have reported the general microstructural features of the silicon nitride/silicon carbide composite as: silicon nitride and silicon carbide grains of ~200nm form a dual phase matrix, SiC particles of 10~30nm were included in some of the silicon nitride grains.

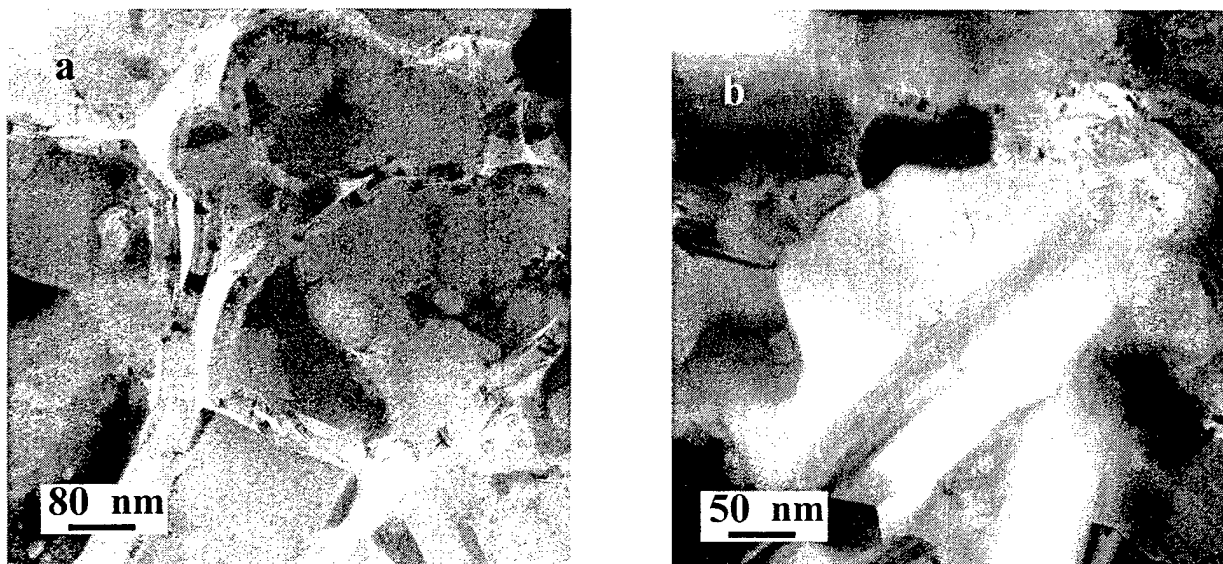
Phase identification of crystalline consolidated specimens was determined using X-ray diffraction. Microstructural evolution and crystalline grain size were examined by transmission electron microscopy (TEM). General microstructural evaluations were performed on a Philips CM12 operating at 120kV. High resolution TEM work was performed at the National Center for Electron Microscopy (NCEM) in Berkeley, CA, using a Philips CM200 FEG operating at 200kV. Chemistry of the grains and grain boundary phases were also determined using the CM200.

The grain boundaries of the nanocomposites were found to be quite different from that of the conventional silicon nitride. Grain-boundaries free of glassy grain boundaries were frequent, and even in boundaries that do contain a glassy phase, the thickness could be extremely narrow as compared to conventional silicon nitride (Fig. 2).



**Fig 2 Grain boundaries in SPSed nanocomposites, without glassy phase (left) and with very thin glassy phase (right)**

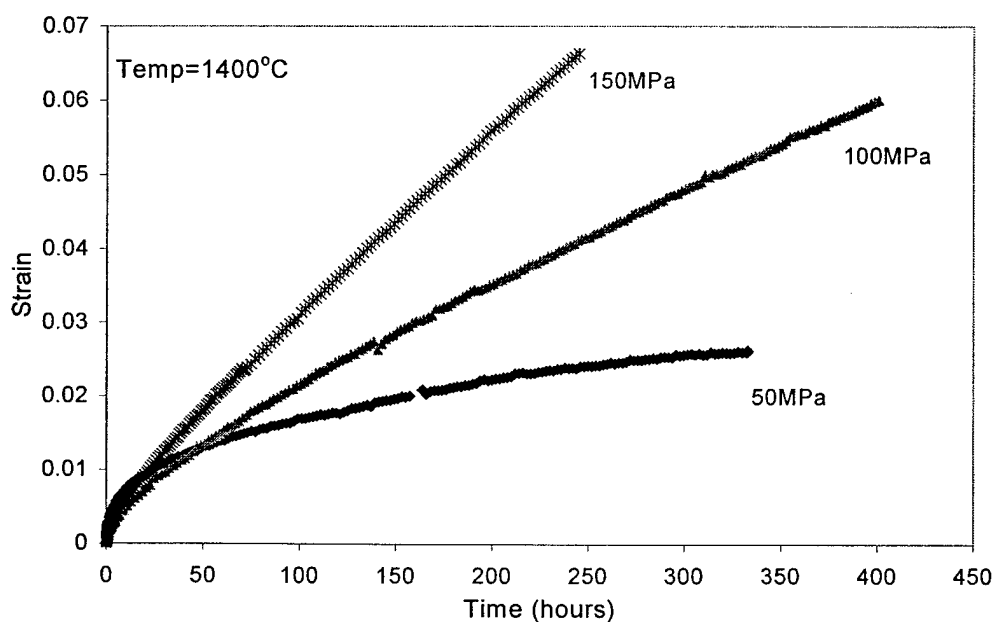
Another important feature of the nanocomposites from sintering of amorphous Si-C-N is the existence of turbostratic graphite, which is a result of the excess carbon content in the Si-C-N starting powder as compared to stoichiometric composition of silicon carbide and silicon nitride, as can be seen in Fig. 3. Most of the graphite phase exists at the intergranular regions of the crystalline phases, and sometimes even form continuous cages that enclose either a single crystalline grain or a group of grains (Fig. 3(a)). Other times it might form large pockets that have a comparable size with the crystalline grains, and small clusters of the graphite phase can be found as inclusions in a crystalline grain (Fig. 3(b)).



**Fig. 3 Graphitic phase in the nanocomposites**  
(a) intergranular (b) intragranular

## 2. Creep characteristics

So far, only batches NH0W, NH0F and NH400 have been tested on their creep behavior. A typical creep curve ( $\epsilon$ -versus-time) is shown in Figure 4 for three different stresses during a constant temperature test. Under constant stress, all materials exhibited a short period of transient creep followed by a decrease in the creep rate. For stresses above 100MPa, samples reached steady state after  $\sim 150$  hours of creep.



**Fig. 4 – Creep curves for sample NH0F tested at 1400°C**

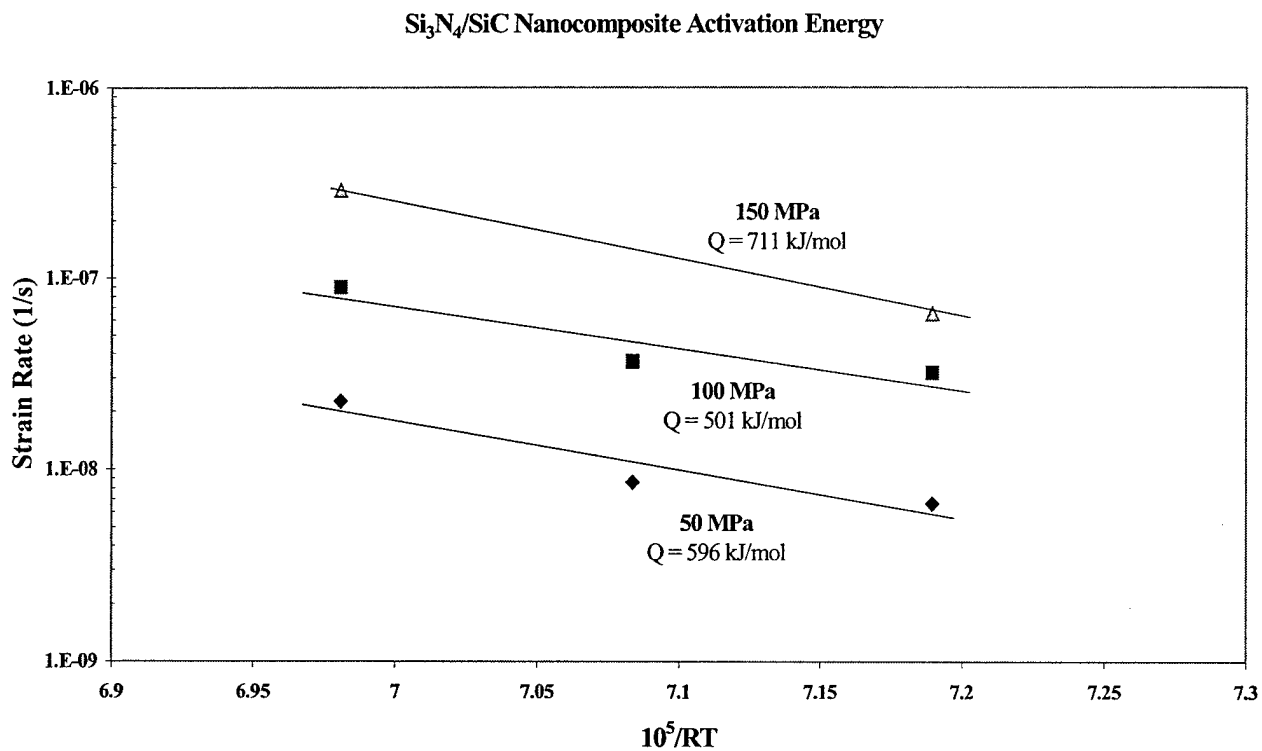
Creep rates at the end of testing (secondary creep) were related to stress and temperature using the Dorn-Boltzman relation:

$$\dot{\epsilon} = A d^{-p} \sigma^n \exp(-Q/RT) \quad [1]$$

where, A is as constant, d the mean grain size, p the grain size exponent,  $\sigma$  the stress, n the stress exponent, Q the apparent activation energy, R the gas constant and T the absolute temperature.

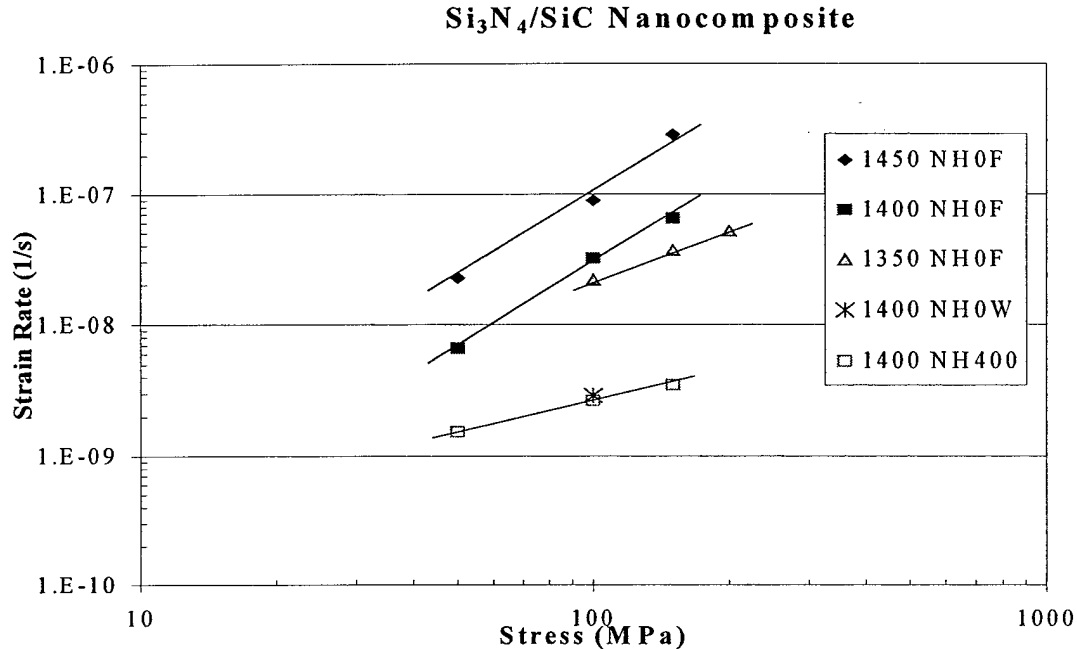
Plots of strain rate-vs-temperature were used to determine activation energy. As an example shown in Fig. 5, the activation energy of the creep deformation is within 400~800kJ/mol, differing with material and stress range. These values are consistent with literature values of activation energy.

Plots of creep rate-vs-stress were used to determine stress exponent, which is another parameter crucial for revealing deformation mechanism (Fig. 6). The stress exponent has values 0.7 and 2. n value of 1 and 2 indicates a creep mechanism of solution-precipitation controlled by either diffusion through glassy phase, or the solution or precipitation reaction at glass/crystal boundaries.  $n < 1$  means that a shear thickening effect of the glassy phase is involved in the creep deformation.



**Fig. 5 - Determination of activation energy of creep**

Fig. 6 also gives a comparison of the creep rate level between these three batches of materials tested. At the same temperature and under the same stress, the material experienced WC high energy ball milling rather than iron ball milling which shows creep rate roughly an order of magnitude lower.



**Fig. 6 Determination of stress exponent of creep**

Ammonia treatment at 400°C apparently improves the creep resistance of the material. This could be assignable to the decrease in free graphite in the grain boundary regions. However, since the role of graphite in the creep process is not yet clear, this remains a hypothesis and will be one of the major subjects of the research in the remaining time of this project.

It should be pointed out that, the results in Fig. 5 and Fig. 6 summarized the currently available data, and are obviously not adequate for conclusively determining  $Q$  and  $n$  values. More data points are being collected for these two figures and the values of activation energy and stress exponent are subject to change as more data allows more accurate calculation.